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I, KIM MARSHALL, MANAGER EXAMINATION SUPPORT AND SALES, hereby certify that the annexed is a true copy of the Provisional specification in connection with Application No. PO 9950 for a patent by SOLA INTERNATIONAL HOLDINGS LTD. filed on 21 October 1997.

I further certify that the annexed specification is not, as yet, open to public inspection.

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KIM MARSHALL
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Patents Act 1990

PROVISIONAL SPECIFICATION

APPLICANT : **SOLA INTERNATIONAL HOLDINGS LTD.**

TITLE : **SURFACE COATING COMPOSITION**

This invention is described in the following statement:

SURFACE COATING COMPOSITION

The present invention relates to a surface coating composition in particular a light-absorbing coating, and to optical articles bearing such coatings.

The optical articles according to the present invention are preferably employed in the preparation of articles such as optical lenses, including spectacle lenses, including sunglass lenses, visors, shields, glass sheets, protective screens, and the like.

As is known in the prior art, tinted sunlenses are most often produced by dipping transparent substrates (either uncoated or with a tintable hard coat) in a hot bath containing a dye solution, which is imbibed into the surface of the lens. If a reflective mirror coating is desired, the tinted substrate is then cleaned and coated in an evaporative box coater. Such multi-stage processes are both time-consuming and expensive. For laminated lens wafer systems, for example of the Matrix-type, liquid bath tinting is not a desired option - it is a low yield process involving significant handling and possible distortion of fragile wafers. Such tinted lenses may also exhibit poor abrasion and scratch resistance and variable depth of colour.

Moreover, for sunglass lenses in particular, it would be a significant advance in the art if reflection of visible light at the concave (or rear) lens surface could be kept sufficiently low to avoid glare from incident light at the concave surface.

Accordingly, it is an object of the present invention to overcome, or at least alleviate, one or more of the difficulties or deficiencies related to the prior art.

Accordingly, in a first aspect of the present invention there is provided a coated optical article including

an optically clear article; and

a light-absorbing coating deposited on at least one surface of the optically clear article; the light-absorbing coating including a plurality of overlapping light absorbing and generally transparent layers, and wherein the thickness and/or number of the respective layers are selected to provide a tinted optical article.

Desirably, the tinted optical article exhibits an anti-reflective effect on the eye side of the optical article.

The coated optical article according to the present invention has the advantage that as the coating is deposited on the surface of the article, the coating may function both as an anti-reflection coating and tinted coating without the need for an additional tinting step. Further the deposited coating may exhibit much improved adhesion and thus improved abrasion resistance.

The optically clear article may be a sunglass lens, ophthalmic lens element, visor or the like. An ophthalmic lens element is preferred.

By the term "ophthalmic lens element" we mean all forms of individual refractive optical bodies employed in the ophthalmic arts, including, but not limited to, lenses, lens wafers and semi-finished lens blanks requiring further finishing to a particular patient's prescription. Also included are formers used in the manufacture of progressive glass lenses and moulds for the casting of progressive lenses in polymeric material such as the material sold under the trade designation CR39.

Where the optically clear article is an ophthalmic lens element, the thickness and/or number of the respective layers may be selected to provide an anti-reflection effect on the eye side or wearer side of the lens.

Where the optically clear article is an ophthalmic lens element, the ophthalmic lenses may be formed from a variety of different lens materials, and particularly from a number of different polymeric plastic resins. A common ophthalmic lens material is diethylene glycol bis (allyl carbonate). Lens materials with higher refractive indices are now growing in popularity. One such material is a CR39 (PPG Industries). Other high index lens materials are based on acrylic or allylic versions of bisphenols or allyl ophthalates and the like. Other examples of lens materials that may be suitable for use with the invention include other acrylics, other allylics, styrenics, polycarbonates, vinylics, polyesters and the like. The lens material "Spectralite" of Applicants is particularly preferred.

The optical article may be formed from cross-linkable polymeric casting compositions, for example as described in the Applicants United States Patent 4,912,155, United States Patent Application No. 07/781,392, Australian Patent Applications 50581/93 and 50582/93, and European Patent Specification 453159A2, the entire disclosures of which are incorporated herein by reference.

For example, in Australian Patent Application 81216/87, the entire disclosure of which is incorporated herein by reference, the Applicant describes a cross-linkable casting composition including at least polyoxyalkylene glycol diacrylate or dimethacrylate and at least one poly functional unsaturated cross-linking agent.

Further, in Australian patent Application 75160/91, the entire disclosure of which is incorporated herein by reference, the Applicants describe a polyoxyalkylene glycol diacrylate or dimethacrylate; a monomer including a recurring unit derived from at least one radical-polymerisable bisphenol monomer capable of forming a homopolymer having a high refractive index of more than 1.55; and a urethane monomer having 2 to 6 terminal groups selected from a group comprising acrylic and methacrylic groups.

Where the optically clear article is a lens element, preferably an ophthalmic lens element, the light absorbing coating may be deposited on the front and/or rear surface of the lens. Desirably the coating may be deposited on the front (convex) surface only.

The light absorbing coating may be formed from overlapping light absorbing and generally transparent layers, as discussed above. Desirably the light absorbing coating is formed from alternating transparent and absorbing layers.

The number and/or thickness of the light absorbing and generally transparent layers may be selected to provide an eye side anti-reflective coating utilising suitable computer software.

The transparent layers may be formed from any suitable optically clear material. The transparent layers may be formed of a dielectric material. Preferably the dielectric layers may be formed from metal oxides, fluorides or nitrides. Metal oxides which may be used for forming transparent layers include one or more of SiO, SiO_2, ZrO_2, Al_2O_3, TiO, TiO_2, Ti_2O_3, Y_2O_3, Yb_2O_3, MgO, Ta_2O_5, CeO_2 and HfO_2. Fluorides which may be used include one or more of MgF_2, AlF_3, BaF_2, CaF_2, Na_3AlF_6, Ta_2O_5, and $Na_5Al_3Fl_{14}$. Suitable nitrides include Si_3N and AlN.

A silica (SiO_2) material is preferred.

In a particularly preferred embodiment, the first deposited layer may be a silica layer followed by alternating light absorbing and generally transparent,

preferably silica, layers. The transparent dielectric layers may be substantially thicker than the light absorbing or metallic layers. The first layer may be of approximately 10 to 75 nm, preferably approximately 25 to 60 nm. This first layer may provide significant improvement in the abrasion resistance of the multi-layer coating.

The generally transparent layers within the body of the light absorbing coating may be relatively thick. The thicknesses may be such as to generate interference effects which substantially cancel out internal reflections. Thicknesses of for example from approximately 20 nm to 100 nm, preferably approximately 25 nm to 85 nm may be used.

The generally transparent layers may in a preferred embodiment exhibit a reducing thickness towards the outer surface of the light absorbing coating. The outer dielectric layers may be from approximately 5 nm to 50 nm, preferably approximately 10 nm to 40 nm in thickness.

The light absorbing layers of the light absorbing coating may be formed from any suitable material. Metals, metal oxides or nitrides may be used.

Desirably a metallic layer may be selected to provide a generally neutral, e.g. grey transmission. Accordingly a silver-coloured metal, e.g. niobium (Nb), Chromium (Cn), Tungsten (W), Tantalum (Ta), Tin (Sn), Palladium (Pd) or Titanium (Ti) or mixtures thereof may be used. Niobium (Nb) is preferred.

The combination of light absorbing and transparent layers may provide a bright, coloured reflection when viewed from the front of a lens. A mirror type coating may be produced.

The thickness of the light absorbing layers may be such as to attenuate transmitted light. The light absorbing or metallic layers may generally be of a substantially reduced thickness relative to the transparent or dielectric layers. The light absorbing layers may be from approximately 1 nm to 10 nm, preferably approximately 2 nm to 5 nm in thickness.

In a preferred form, the light absorbing coating may include a total 4 to 12 alternating light absorbing-generally transparent layers, preferably 6 to 8 alternating layers. An additional primer layer may be included, as discussed above.

Figure 1 illustrates the optical properties of the light absorbing coating according to the present invention. In Figure 1a, the reflective and transmissive performance for light incident from the front of the lens is shown. Note that when viewed from the front, the reflection from the back surface of the lens is so weak that it can be ignored. Figure 1b depicts the performance of the lens for light incident from the rear, such as would be the case for side glare or reflections of the wearer's eyes. The mirror/tint coating acts as an anti-reflective surface, minimising the intensity of undesired reflections. Note that reflections also arise from the back surface of the lens. This surface may be coated with a conventional AR coating (e.g. the back surface of back wafers generally have a standard AR-coating), so reflections from this surface can be ignored for the purpose of this work.

The coatings are preferably based on an 8-layer Nb/SiO_2 multi-layer structure to provide broadband anti-reflection from the wearer side.

The resultant coating may exhibit a silver mirror-type appearance. Alternatively the light absorbing coating may be modified to produce a different colour coating. For example a metallic oxide, e.g. niobium oxide coating may be applied. A combination of dielectric top coatings may be applied. A combination of a silica coat and a niobia coat is preferred. A silica top coat may be added to modify colour and additionally enhance abrasion resistance.

The coated optical article may further include one or more additional coatings. Accordingly in a further aspect of the present invention there is provided a multi-coated optical article including

an optical article; and

a light-absorbing coating deposited on at leat one surface of the optically clear article; the light-absorbing coating including a plurality of overlapping light absorbing and generally transparent layers, and wherein the thickness and/or number of the respective layers being selected to provide a tinted optical article, and

an optically clear secondary coating which provides a desirable optical and/or mechanical property to the optical article, which coating may underlay or overlay the light absorbing coating.

Desirably, the tinted optical article exhibits an anti-reflective effect on the eye side of the optical article

The secondary coating may be of any suitable type. The secondary coating may be one or more of an anti-reflective abrasion resistant or impact-resistant coating. An abrasion-resistant coating is preferred. The combination of an abrasion resistant coating and an anti-reflective coating is particularly preferred.

An abrasion-resistant (hard) coating including an organosilicone resin is preferred. A typical organosilicone resin that is suitable for use in the present invention has a composition comprising one or more of the following:

1) organosilane compounds with functional and/or non-functional groups such as glycidoxypropyl trimethoxy silane;
2) co-reactants for functional groups of functional organosilanes, such as organic epoxies, amines, organic acids, organic anhydrides, imines, amides, ketamines, acrylics, and isocyanates; colloidal silica, sols and/or metal and non-metal oxide sols; catalysts for silanol condensation, such as dibutylin dilaurate;
3) solvents such as water, alcohols, and ketones;
4) other additives, such as fillers;

Abrasion resistant coats of acrylic, urethane, melamine, and the like may also be used. These materials, however, frequently do not have the good abrasion resistant properties of organo-silicone hard coatings.

The abrasion-resistant (hard) coating may be coated by conventional methods such as dip coating, spray coating, spin coating, flow coating and the like. Coating thicknesses of between approximately 0.5 and 10 microns are preferred for abrasion and other properties.

The front and/or rear lens surfaces may include an abrasion resistant coating. e.g. of the type described in United States Patent 4,954,591 to the Applicants, the entire disclosure of which is incorporated herein by reference.

In a preferred aspect, one or both surfaces of the optical article may be subjected to a surface treatment to improve bondability and/or compatibility of the light absorbing and/or secondary coating. The surface treatment may be selected from one or more of the group consisting of plasma discharge, corona discharge,

glow discharge, ionising radiation, UV radiation, flame treatment and laser, preferably excimer laser treatment. A plasma discharge treatment is preferred. The surface treatment, alternatively or in addition, may include incorporating another bonding layer, for example a layer including a metal or metal compound selected from the group consisting of one or more of Chromium, Nickel, Tin, Palladium, Silicon, and/or oxides thereof.

The front and/or rear lens surfaces may further include one or more additions conventionally used in casting compositions such as inhibitors, dyes including thermochromic and photochromic dyes, polarising agents, UV stabilisers and materials capable of modifying refractive index.

Accordingly the optical article may be of the type described in International Patent Application PCT/AU96/00704 and PCT/AU96/00705 "Light Transmissible Articles with Colour Enhancing Properties" and "Light Transmissible Article with Reduced Ultraviolet Transmission", respectively to the Applicants, the entire disclosures of which are incorporated herein by reference.

The optical article may be a sunglass lens of the wrap-around or visor type, for example of the type described in International Patent Application PCT/AU97/00188 "Improved Single Vision Lens" to Applicants, the entire disclosure of which is incorporated herein by reference.

In a further aspect of the present invention, there is provided a method for preparing a coated optical article as described above, which method includes

providing

an optical article,

a light absorbing material,

a generally transparent material;

depositing overlapping layers of light absorbing material and generally transparent material on a surface of the optical article, the number and/or thickness of the respective layers being selected to provide a tinted optical article.

The deposition step may be a vacuum deposition step. The deposition step may be conducted in a coating apparatus. A box coater or sputter coater may be used.

In a preferred aspect the light absorbing or metallic material and generally transparent or dielectric material, preferably Nb and SiO_2, are deposited as

alternating layers.

The light absorbing coating may preferably be formed on the surfaces of the substrate according to the process and the box coaters as described in the Italian Patent No. 1.244.374 the entire disclosure of which is incorporated herein by reference.

In accordance with said procedure, the various layers of the light absorbing coating may be deposited in subsequent steps utilising a vacuum evaporation technique and exposing the growing layers to a bombardment of a beam of ions of inert gas.

Moreover, in accordance with the preferred process, the deposition of the layers may be achieved at a low temperature (generally below 80°C), using an ion beam having a medium intensity (meaning the average number of ions that reach the substrate) included between approximately 30 and 100 μA/cm2 and the energy included between approximately 50 and 100 eV.

Preferably, the optical article is maintained at an elevated temperature during the deposition of the various layers of the light absorbing coating.

According to the present invention it has been found that, following the procedures mentioned above, it is possible to achieve a relatively thin, light absorbing coating with consequent advantages in both optical and mechanical properties.

In a further preferred aspect of the present invention, there is provided a coated lens element including

a lens wafer having

a first lens surface, and

a second lens surface,

the first or second lens surface having deposited thereon a light absorbing coating deposited on at least one surface of the optically clear article; the light-absorbing coating including a plurality of overlapping light absorbing and generally transparent layers;

the thickness and/or number of the respective layers being selected to provide a tinted lens element.

Desirably, the tinted optical article exhibits an anti-reflective effect on the eye side of the optical article

The coated lens wafer may be a front surface wafer or a rear surface wafer. Where the coated lens wafer is a front surface wafer the light absorbing coating may be deposited on the first (front) or second (rear) lens surface thereof.

Where the coated lens wafer is a rear surface wafer, the light absorbing coating is preferably deposited on the first (front) surface thereof.

Accordingly in a still further aspect of the present invention, there is provided a laminate optical article including

a front lens wafer including

a first lens surface; and

a second lens surface

a complementary back lens wafer adhered thereto, including a first and second lens surface; and

a light absorbing coating deposited on a contact surface therebetween, the light absorbing coating including a plurality of overlapping light absorbing and generally transparent layers;

the thickness and/or number of the respective layers being selected to provide a tinted lens element.

It will be understood that, in this embodiment, in addition to the advantages of the present invention described above, the light absorbing coating provided is protected by the optical lens wafers themselves and is thus virtually indestructible.

In addition, abrasion resistant and like coatings of the type described above may be applied to the external surfaces of the laminate optical article.

The laminate optical article may be fabricated in a manner similar to that described in International Patent Application PCT/AU96/00805, "Laminate Article", to Applicants, the entire disclosure of which is incorporated herein by reference.

Further characteristics and advantages of the present invention will be apparent from the following description of a few examples of embodiments of the present invention, given as indicative but not restrictive.

EXAMPLE 1

Deposition Procedure

All light absorbing coatings were deposited on first quality, hard coated CR39 lens wafers using a sputter deposition facility.

Substrates were cleaned by wiping with an acetone-soaked tissue. Dust was removed with an air gun before the samples were loaded into the vacuum chamber.

The convex, front surface of the lens wafers were given thirty seconds of plasma exposure (to enhance coating adhesion) before deposition of an initial 50 nm silica layer (which enhanced abrasion resistance as measured in the Bayer abrasion test). Subsequently, eight alternating metal (niobium) and dielectric (silica) layers were deposited to form a low-reflectance tint. For non silver-coloured samples, a niobia and an additional silica layer were added in order to produce a coloured front reflection.

The structures formed are summarised in Table 1.

TABLE 1

Layer			Mirror colour and layer thicknesses (nm)				
Number	Material	Primary function	Silver	Gold	Blue	Metallic blue	Black
Substrate							
1	SiO_2	Scratch resist	50	50	50	50	50
2	Nb	Absorption	2	2	2	2	2
3	SiO_2	Back AR	80	80	80	80	80
4	Nb	Absorption	4	4	4	4	4
5	SiO_2	Back AR	80	80	65	65	65
6	Nb	Absorption	4	4	4	4	4
7	SiO_2	Back AR	40	40	20	20	20
8	Nb	Absorption	4	4	4	4	4
9	SiO_2	Back AR, front colour	25	10	40	50	10
10	Nb_2O_5	Front colour		10	30	35	30
11	SiO_2	Front colour, scratch resistant		30	30	35	60
			289	314	329	349	349

Table 1: Multi-layer composition of light absorbing coatings

Optical Performance

Transmission Characteristics and ANSI Standards

The light absorbing coatings generally exhibited a neutral transmission, except for the blue coatings, which were slightly yellow in transmission. See Table 2. This is a consequence of the high blue reflectance, which necessarily makes the transmitted light appear more yellow (since less of the blue portions of the spectrum are present).

TABLE 2

Transmission	Silver	Gold	Blue	Metallic blue	Black
Luminous transmittance (%)	10.6	11.3	13.5	11.6	11.4
CIE x coordinate (D65 ill.)	0.33	0.33	0.37	0.36	0.34
CIE y coordinate (D65 ill.)	0.33	0.33	0.37	0.36	0.34
Av. UVB transmittance (%)	0.3	0.5	0.2	0.2	0.3
Av. UVA transmittance (%)	3.4	4.1	2.2	2.2	3.4
Red traffic signal trans. (%)	12.2	12.9	16.9	15.4	13.4
Yellow traffic signal trans (%)	11.2	11.9	14.9	13.1	12.2
Green traffic signal trans. (%)	10.2	11.0	12.7	10.6	10.9
ANSI Standard Z80.3 - 1986	✓	✓	✓	✓	✓

Table 2: Transmittance of lens wafers with light absorbing coating

Due to the metal layers, the light absorbing coatings offer far superior infra-red blocking compared to that obtained from a typical dye-tinted lens, as seen in Figure 2.

Reflectance

Table 3 shows the reflectance from the front and wearer sides of the light absorbing mirror/tint coatings (see Figure 1 for reference). (The measurement of the wearer-side reflectance has been corrected to remove the contribution of the uncoated side of the substrate (the back surface of the front wafer), leaving the contribution of the coated surface only. In practice, there is no reflection from the uncoated surface when the front wafer is laminated to an AR-coated back wafer). Figure 3 is a CIE 1931 (x,y) colour chart.

TABLE 3

Coating reflectance (front and wearer sides)	Silver	Gold	Blue	Metallic blue	Black
Front side					
Luminous reflectance (%)	16.3	11.4	10.2	23.3	3.5
CIE coordinate (D65 ill.), x	0.32	0.35	0.20	0.24	0.31
CIE coordinate (D65 ill.), y	0.34	0.37	0.21	0.26	0.31
Wearer side					
Luminous reflectance (%)	~0.10	~0.40	~0.20	~0.10	~0.55
CIE coordinate (D65 ill.), x	0.12	0.18	0.20	0.13	0.21
CIE coordinate (D65 ill.), y	0.10	0.16	0.15	0.10	0.19

Table 3: Reflectance of light absorbing mirror/tint coated lens wafers

The "mirror" coatings have a luminous front reflectance of 10% or more. This is enough to appear reflective, without fully obscuring the wearer's eyes. A lower reflectance coating, such as the "black" coating, is perceived to have colour, but not to act as a "mirror". The "black" coating resembles a black, tinted substrate, without a "mirror".

From the wearer-side reflectances, it is clear that the coatings are all quite anti-reflective from the rear - for comparison, a standard anti-reflective coating has a luminous reflectance of ~0.50%. As given by the chromaticity coordinates, the wearer-side reflections of the light absorbing mirror/tint coatings are all deep-blue to purple in colour.

Table 4 provides comparisons of abrasion and durability tests conducted on standard sun lenses and lenses according to the present invention.

TABLE 4

Abrasion/durability test	18 Various standard mirrors, various tints, on CR39 planos	3 Silver mirror/tints on hard-coated CR39 lens wafers
Primary adhesion	0-5 (0=words, 5=best)	5,5,5
Steel wool abrasion	All 1 (0=worst, 5=best)	5,5,5
Bayer sand abrasion	0.6 - 1.4 (higher=better)	2,1, 2.3, 2.5
Salt water boil	0-5 (0=worst, 5=best)	5,5,5
Simulated outdoor (SEDT)	1-5 (0=worst, 5=best)	5,5,5
Outdoor exposure	All 0 (0=worst, 5=best)	5,5,5

Table 4: Durability and scratch resistance - standard mirrors versus current light absorbing mirror/tint coating on CR39 Matrix wafers.

From Table 4 it is clear that the mirrored sunlens samples of the present invention exhibit outstanding durability and abrasion resistance, far superior to the comparison product. The reason is that the present coating can be deposited on a non-tintable hard coat, whereas other commercially-available products are often mirror coatings on tintable hard coats, which not only are structurally weaker, but also contain organic dyes which can compromise adhesion of the mirror coating.

Finally, it is to be understood that various other modifications and/or alterations may be made without departing from the spirit of the present invention as outlined herein.

DATED: 21 October, 1997

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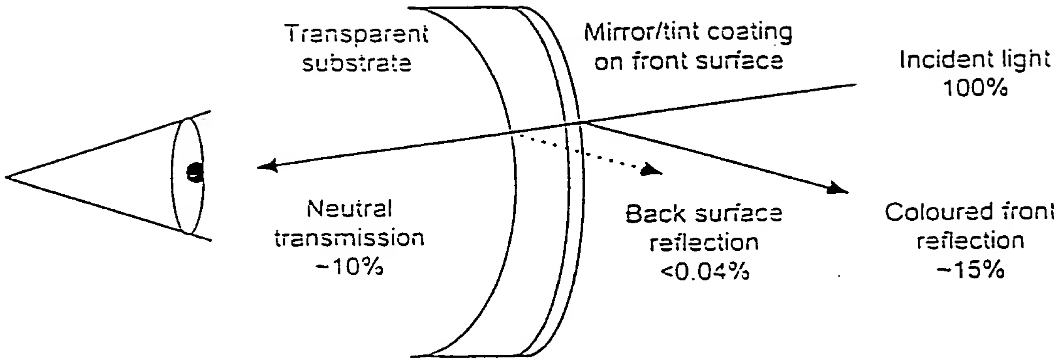

Figure 1a : Performance of light absorbing coating for light incident from front.

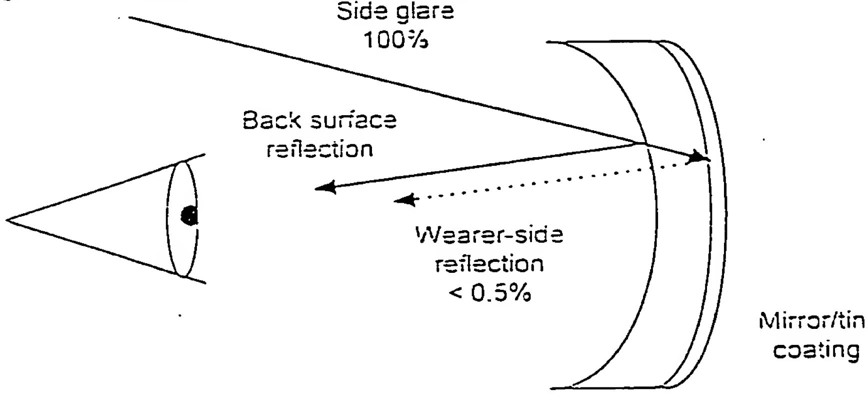

Figure 1b : Performance of light absorbing coating for light incident from wearer side.

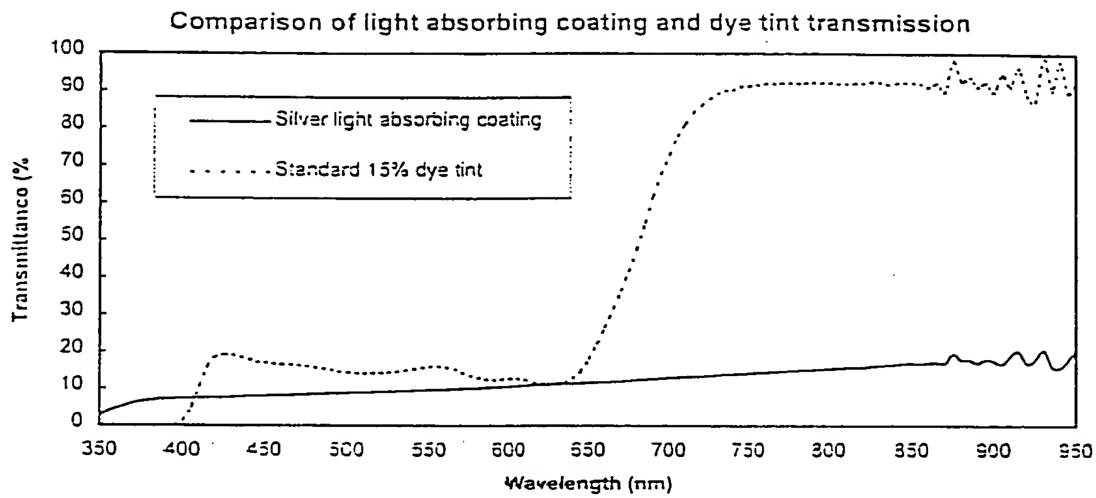

Figure 2 : Transmittance of a lens wafer with light absorbing coating compared to a typical dye-tinted substrate.

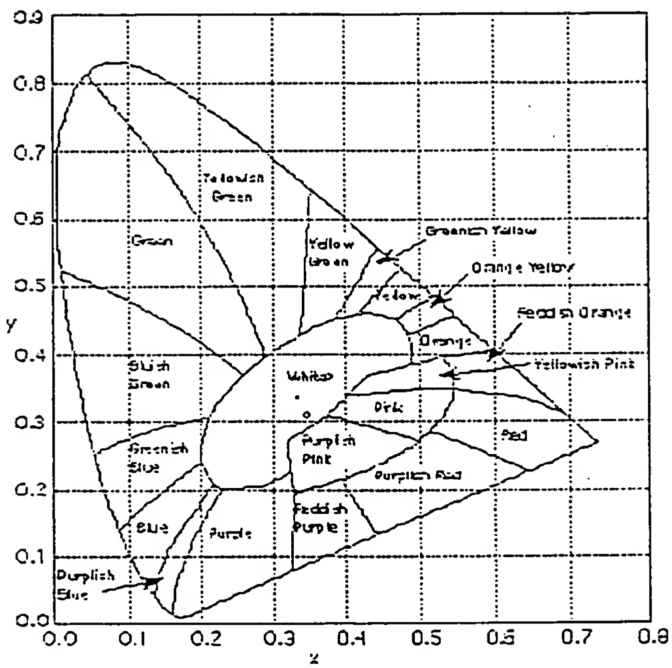

Figure 2 : CIE chromaticity diagram.